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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Aqueous Coating Composition, Its Preparation and Use

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STATE OF THE ART

Water-dilutable coating agents based on aqueous polyurethane dispersions for the preparation of surfacers are known from EP-OS No. 278,394. Polyether polyols having a functionality of at least 3 are used therein as longer-chain polyols for preparing the polyurethane resin and the resulting dispersions are preferably used for improving the use properties of polyester/melamine resin mixtures.

In contrast, German Offenlegungsschrift No. 3,545,618 relates to water-dilutable coating agents based on aqueous polyurethane dispersions for producing the base coat of a multilayer topcoat. To prepare the polyurethane resin, ionic prepolymers containing NCO groups are reacted with polyols containing at least three hydroxyl groups resulting in chain-lengthening and possibly chain branching. Mention of other areas of application than those for base coats is not made in this publication.

OBJECTS OF THE INVENTION

It is an object of the invention to provide aqueous coating compositions for primers and primer surfacers having good interlayer adhesion and improved stone chip resistance and the process for their preparation.

It is another object of the invention to provide coated substrates, especially auto body parts, having improved corrosion protection and stone chip resistance.

These and other objects and advantages of the invention will become obvious from the following detailed description.

The novel aqueous coating compositions of the invention for preparing primers or primer surfacers contain at least one water-dispersible binder resin, and crosslinking agents and optionally conventional additives, wherein at least some of the water-dispersible binder resin is a polyurethane resin containing structural units derived from

(A) polyisocyanates,

(B) polyols having an average molecular weight $\overline{M}_n$ of at least 400,

(C) optionally low-molecular weight polyols,

(D) compounds having at least two groups which are reactive toward isocyanato groups and at least one group which is capable of anion formation,

(E) polyols carrying no other groups which are reactive with isocyanato groups, these structural units (E) being in each case at the chain end of the polyurethane resin,

(F) optionally compounds which are monofunctional or contain active hydrogen of varying reactivity and are different from (E), these structural units (F) likewise being at the chain end of the polyurethane resin and,

(G) optionally compounds which are different from (B), (C), (D), (E) and (F) and contain at least two groups which are reactive with NCO groups.

Surfacer or primer surfacer layer is intended to mean the layer between the primer and topcoat, particularly in automotive bodies or parts thereof, which serve for leveling out uneven places in the primer, which has the function of ensuring flawless appearance of the topcoat and for improving the stone chip resistance of the entire coating. By virtue of its plastic behavior,

tl layer is intended to prevent stone chips and the like, such as are thrown against the coating by other cars or even the car itself, from penetrating the coating. Moreover, the surfacer compositions must produce relatively hard films to permit wet grinding of the coating without giving rise to glazing of the grinding paper.

The polyurethane resin of the invention has generally an average molecular weight $\bar{M}_n$ (calculated from the stoichiometry of the starting material) of 1,600 to 50,000, preferably 1,600 to 10,000 and most preferably 2,000 to 6,000, an acid number of 10 to 80, preferably 25 to 60, and a hydroxyl number of 30 to 200, preferably 50 to 100. It is water-dispersible at least in an alkaline medium and at low molecular weights frequently even water-soluble under these conditions. In general, the structure of the molecule chains of this polyurethane resin is predominantly linear, although in some cases a slight degree of branching of preferably up to 30%, more preferably up to 10%, may be present. The gel content is generally less than 5% by weight, preferably less than 1% by weight. On statistical average, each polymer chain preferably contains at least two, preferably 4 to 6, groups having active hydrogen such as amino and/or OH groups.

The polyisocyanates, preferably diisocyanates, (A) are compounds known in the area of polyurethanes or coatings such as aliphatic, cycloaliphatic or aromatic diisocyanates. They preferably have the formula $Q(NCO)_2$, in which Q is a hydrocarbon of 4 to 40 carbon atoms, preferably 4 to 20 carbon atoms, and is more preferably an aliphatic hydrocarbon of 4 to 12 carbon atoms, a cycloaliphatic hydrocarbon of 6 to 15 carbon atoms, an aromatic hydrocarbon of 6 to 15 carbon atoms, or an araliphatic hydrocarbon of 7 to 15 carbon atoms. Examples of diisocyanates of this type to be used are preferably tetramethylene diisocyanate, hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane,

3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate), 4,4'-diisocyanato-dicyclohexylmethane, 2,2-(4,4'-diisocyanatodicyclohexyl)-propane, 1,4-diisocyanatobenzene, 2,4- or 2,6-diisocyanatotoluene or mixtures of these isomers, 4,4'- or 2,4'-diisocyanatodiphenylmethane, 2,2-(4,4'-diisocyanatodiphenyl)-propane, p-xylylene diisocyanate and a,a,a',a'-tetramethyl-m- or p-xylylene diisocyanate and mixtures of these compounds.

Apart from these simple polyisocyanates, those containing hetero atoms in the group linking the isocyanato groups are also suitable. Examples of these are polyisocyanates having carbodiimido groups, allophonato groups, isocyanurato groups, urethane groups, acylated urea groups or biuret groups. As regards further suitable polyisocyanates, see for example, German Offenlegungsschrift No. 2,928,552.

The polyisocyanate (A) content in the polyurethane resin is usually about 10 to 50% by weight, preferably 25 to 35% by weight, relative to the polyurethane resin.

The polyols of (B) preferably have an average molecular weight $\bar{M}_n$ of 400 to 5,000, more preferably 800 to 2,000. Their hydroxyl number is generally 30 to 280, preferably 50 to 200 and more preferably 80 to 160, mg of KOH/g.

Examples of polyols of this type which are the compounds known from polyurethane chemistry are polyether polyols, polyester polyols, polycarbonate polyols, polyesteramido polyols, polyamido polyols, epoxy resin polyols and their reaction products with CO_2, polyacrylate polyols and the like. Polyols of this type which can also be used in a mixture are described, for example, in German

Offenlegungsschriften No. 2,020,905; No. 2,314,513 and No. 3,124,784 and European Offenlegungsschrift No. 120,466.

Of these polyols, the polyether and polyester polyols are preferred, preferably those having only terminal OH groups and a functionality of less than 3, preferably 2.8 to 2 and most preferably 2.

Examples of suitable polyether polyols are polyoxyethylene polyols, polyoxypropylene polyols, polyoxybutylene polyols and preferably polytetrahydrofuran having terminal OH groups.

The polyester polyols which are particularly preferred in the invention are known polycondensation products of di- and, if appropriate, poly(tri-, tetra)ols with di- and, if appropriate, poly (tri-, tetra)carboxylic acids, or hydroxycarboxylic acids or lactones. It is also possible to use the corresponding polycarboxylic acid anhydrides or the corresponding polycarboxylic acid esters of lower alcohols, instead of the free polycarboxylic acids, for preparing the polyesters. Examples of suitable diols are ethylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyalkylene glycols such as polyethylene glycol, furthermore propanediol, 1,4-butanediol, 1,6-hexanediol, neopentylglycol or neopentylglycol hydroxypivalate, the three last-mentioned compounds being preferred. Examples of suitable polyols which optionally can also be used are trimethylolpropane, glycerol, erythritol, pentaerythritol, trimethylolbenzene or tris(hydroxyethyl)isocyanurate.

Examples of suitable dicarboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexane-dicarboxylic acid, adipic acid, azelaic acid, sebacic acid, glutaric acid, "chlorendic acid",

tetrachlorophthalic acid, maleic acid, fumaric acid, itaconic acid, malonic acid, suberic acid, 2-methylsuccinic acid, 3,3-diethylglutaric acid and 2,2-dimethylsuccinic acid. Anhydrides of these acids are also useful insofar as they exist. Consequently, the anhydrides are also covered by the term "acid". It is also possible to use monocarboxylic acids such as benzoic acid and hexanecarboxylic acid, provided the average functionality of the polyol is higher than 2. Saturated aliphatic or aromatic acids are preferred such as adipic acid or isophthalic acid. A polycarboxylic acid which optionally may additionally be used in relatively small amounts is trimellitic acid.

Examples of hydroxycarboxylic acids which can be used as reactants in the preparation of a polyester polyol having terminal hydroxyl include hydroxycaproic acid, hydroxybutyric acid, hydroxydecanoic acid, hydroxystearic acid and the like. Useful lactones include caprolactone, butyrolactone and the like.

The amount of component (B) in the polyurethane resin is usually between 15 and 80% by weight, preferably 40 to 60% by weight, relative to the polyurethane resin.

The low-molecular-weight polyols (C) which optionally, may be used for synthesizing the polyurethane resins usually have the effect of stiffening the polymer chain. In general, they have a molecular weight of about 60 to 400, preferably 60 to 200, and hydroxyl numbers of, for example, 200 to 1,500. They can contain aliphatic, alicyclic or aromatic groups and the amount thereof is generally 0 to 20, preferably 1 to 10% by weight, relative to polyol components (B) to (D). Examples are the low-molecular-weight polyols having up to about 20 carbon atoms per molecule, for example ethylene glycol, diethylene glycol, 1,2-propanediol, 1-3-

...opanediol, 1,4-butanediol, 1,3-butylene glycol cyclohexanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, bisphenol A (2,2-bis(4-hydroxyphenyl)-propane), hydrogenated bisphenol A (2,2-bis(4-hydroxycyclohexyl)-propane) and mixtures thereof, and as triol trimethylolpropane.

Examples of compounds suitable for structural unit (D) are described in U.S. Patents No. 3,412,054 and No. 3,640,924 and in German Offenlegungsschriften No. 2,624,442 and No. 2,744,544 incorporated herein by reference. In particular, those polyols are suitable, preferably diols, which contain at least one carboxyl group, generally 1 to 3 carboxyl groups per molecule. Sulfo groups are also suitable as groups capable of anion formation. Examples of these are: dihydroxycarboxylic acids such as α,α-dialkylol-alkanoic acids like α,α-dimethylolalkanoic acids such as 2,2-dimethylolacetic acid, 2,2-dimethylolpropionic acid, 2,2-dimethylolbutyric acid, 2,2-dimethylolpentanoic acid, dihydroxy-succinic acid and polyhydroxy acids such as gluconic acid. Of these, 2,2-dimethylolpropionic acid is particularly preferred. Examples of amino-containing compounds (D) are α,δ-diaminovaleric acid, 2,4-diaminotoluene-5-sulfonic acid and the like. Mixtures of the compounds (D) can also be used and the amount of component (D) in the polyurethane resin is generally 2 to 20, preferably 4 to 10% by weight, relative to the polyurethane resin.

The polyurethane resins used in the invention also contain structural units (E) which are predominantly, preferably to the extent of 70 to 90%, each present at the chain ends and terminate them (chain terminators). Suitable polyols here are those having at least three, preferably 3 or 4, hyroxyl groups. Examples are glycerol, hexanetriol, pentaerythritol and trimethylolpropane, the latter being preferred. The amount of (E) is usually between 2 and 15, preferably 5 to 15% by weight, relative to the polyurethane

in. If desired, these structural units(E) are present in the polyurethane resin in a mixture with structural units (F).

The structural units(F) are derived from monofunctional compounds which are reactive with NCO groups such as monoamines, particularly secondary monoamines or monoalcohols. Examples are methylamine, ethylamine, propylamine, butylamine, octylamine, laurylamine, stearylamine, isononyloxypropylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, N-methylaminopropylamine, diethyl(methyl)aminopropylamine, morpholine, piperidine, or suitably substituted derivatives thereof, amidoamines from primary diamines and monocarboxylic acids, monoketimines of primary diamines, primary/tertiary amines such as N,N-dimethylaminopropylamine and the like.

Preferably, suitable compounds for (F) are those containing active hydrogen of varying reactivity toward NCO groups such as compounds having, apart from a primary amino group, also secondary amino groups, or, apart from an OH group, also COOH groups, or, apart from a primary or secondary amino group, also OH groups, the latter being preferred. Examples of these are: primary/secondary amines such as 3-amino-1-methylaminopropane, 3-amino-1-ethylaminopropane, 3-amino-1-cyclohexylaminopropane, 3-amino-1-methylaminobutane; monohydroxycarboxylic acids such as hydroxyacetic acid, lactic acid or malic acid, and alkanolamines such as N-aminoethylethanolamine, ethanolamine, 3-aminopropanol, neopentanolamine and particularly preferably diethanolamine.

In this manner, functional groups are additionally incorporated in the final polymer product which is thus made more reactive toward materials such as curing agents. The amount of (F) in the polyurethane resin is usually between 2 and 20, preferably

3 and 10% by weight, relative to the polyurethane resin.

In addition to the structural units according to (E) and (F), the polyurethane resin of the invention can optionally also contain structural units (G) which are derived from so-called chain-lengthening agents, although this variation is less preferred. Compounds which are suitable for this are the known compounds which are reactive toward NCO groups and are preferably difunctional compounds not identical with (B), (C), (D), (E) and (F) and in most cases having average molecular weights of up to 400. Examples are water, hydrazine, poly(di)amines such as ethylenediamine, diaminopropane and hexamethylenediamine which can also carry substituents such as OH groups. Polyamines of this type are described, for example, in German Offenlegungsschrift No. 3,644,371. The amount of (G) in the polyurethane resin is usually between 1 and 10, preferably 2 and 5% by weight, relative to the polyurethane resin.

The polyurethane resin of the invention is preferably prepared in such a manner that first a polyurethane prepolymer is prepared from the polyisocyanates of (A), the polyols of (B) and optionally the low-molecular-weight polyols of (C) and the compounds of (D), which prepolymer contains on average at least 1.7, preferably 2 to 2.5, free isocyanato groups per molecule, the prepolymer is then reacted with a stoichiometric excess of the compounds of (E), if desired in a mixture with (F) and/or (G), in a non-aqueous system, and the completely reacted polyurethane resin is then preferably neutralized and transferrd into an aqueous system. If desired, the reaction with (G) can also take place after transfer into the aqueous system.

The preparation of the polyurethane prepolymer is carried out by known processes in which the polyisocyanate is used in excess, relative to polyols (B) to (D), resulting in a product having free isocyanato groups. These isocyanato groups are terminal and/or pendant, preferably terminal. Advantageously, the amount of polyisocyanate is such that the equivalent ratio of isocyanato groups to the overall number of OH groups in polyols (B) to (D) is 1.05 to 1.4, preferably 1.1 to 1.3.

The reaction for preparing the prepolymer is usually carried out at temperatures of 60 to 95°C, preferably 60 to 75°C, depending on the reactivity of the isocyanate used, as a rule, in the absence of a catalyst, but preferably in the presence of solvents inert toward isocyanate. In particular, those solvents are suitable for this which are water-compatible such as the ethers, ketones and esters mentioned below and N-methylpyrrolidone. The amount of this solvent advantageously does not exceed 20% by weight, and is preferably in the range of 5 to 15% by weight, in each case relative to the sum of polyurethane resin and solvent. Advantageously, the polyisocyanate is slowly added to the solution of the other components.

The prepolymer or its solution is then reacted with the compound of (E), if desired in a mixture with (F) and/or (G), the temperature being advantageously in the range of 50 to 100°C, preferably between 60 and 90°C, until the NCO content in the prepolymer has virtually dropped to zero. For this purpose, compound (E), if desired together with (F) and/or (G)is used in excess. The amount of (E) is advantageously such that the equivalent ratio of NCO groups of the prepolymer, which previously may already have been reacted with compounds according to (F) and/or (G), to reactive groups of (E) is 1:1.1to 1:5, preferably 1:1.5 to 1:3. The amount

of (F) and/or (G) can be 0 to 90 %, preferably 0 to 20 %, relative to (E).

A portion of the (unneutralized) COOH groups, preferably 5 to 30% can, if desired, be reacted with difunctional compounds which are reactive with COOH groups such as diepoxides.

For neutralizing the resulting product preferably containing COOH groups, in particular tertiary amines are suitable. Examples are trialkylamines having 1 to 12, preferably 1 to 6 carbon atoms in each alkyl. Examples of these are trimethylamine, triethylamine, methyldiethylamine, tripropylamine. The alkyls can also carry, for example, hydroxyl groups as in the case of dialkylmonoalkanolamines, alkyldialkanolamines and trialkanolamines. An example of these is dimethylethanolamine which preferably serves as neutralizing agent. Neutralizing agents which may also be used are inorganic bases such as ammonia or sodium hydroxide and potassiuim hydroxide.

In most cases, the neutralizing agent is used in a molar ratio of about 0.3:1 to 1.3:1, preferably about 0.5:1 to 1:1, relative to the COOH groups of the prepolymer. The neutralization, which, as a rule, is carried out between room temperatures and 80°C, preferably 40 to 80°C can be carried out in any desired manner, for example by adding the water-containing neutralizing agent to the polyurethane resin or vice versa. However, it is also possible first to add to the polyurethane resin the neutralizing agent and only then the water. In general, this gives solids contents of 20 to 70%, preferably 30 to 50%.

The polyurethane resin content in the aqueous coating composition is generally 5 to 40, preferably 15 to 30% by weight, relative to the entire coating composition.

Apart from the polyurethane resin, the aqueous coating composition can also contain, as binder, up to 60, preferably up to 30% by weight, relative to the polyurethane resin, of other oligomeric or polymeric materials such as crosslinkable, water-soluble or water-dispersible phenolic resins, polyester resins, epoxy resins or acrylic resins and the like as described in European Offenlegungsschrift No. 89,497.

Furthermore, excess polyol of (E) is usually present in the coating composition of the invention, in most cases in amounts of 1 to 10%, preferably 2 to 5% by weight, relative to the polyurethane resin.

Suitable crosslinking agents are the curing agents customary for polyol resins as long as they are water-compatible. Examples are water-compatible (water-soluble or water-dispersible) amino resins, particularly commercially available etherified melamine/formaldehyde condensation products such as hexamethoxymethylmelamine, phenolic resins or capped polyisocyanates as described in German Offenlegungsschrift No. 3,644,372. The amount of crosslinking agent is usually 10 to 35% by weight, preferably 15 to 25% by weight, relative to the sum of binder to be crosslinked and crosslinking agent.

The aqueous coating compositions of the invention, whose pH is in most cases in the range of about 6.0 to 10.0, preferably 6.8 to 8.5, can additionally contain conventional paint additives such as pigments and fillers, and paint additives, for example anti-settling agents, antifoams and/or wetting agents, flow-improving agents, reactive thinners, plasticizers, catalysts, dissolution aids, thickeners and the like. At least part of these additives do not have to be added to the coating composition until immediately

b. ore processing. The selection and dosage of these substances which can be added to the individual components and/or the entire mixture are known to one skilled in the art.

Examples of suitable pigments are iron oxides, lead oxides, lead silicates, titanium dioxide, barium sulfate, zinc oxide, zinc sulfide, phthalocyanine complexes and the like, and suitable fillers are mica, kaolin, chalk, quartz powder, asbestos powder, slate powder, various silicas, silicates and talc, including so-called micro-talc having a maximum particle size of 10 µm (cf. European Offenlegungsschrift No. 249,727). These pigments and/or fillers are usually used in amounts of 10 to 70, preferably 30 to 50% by weight, relative to the overall solids content of the coating composition.

Suitable catalysts are the conventional acid curing catalysts such as p-toluenesulfonic acid, dodecylbenzenesulfonic acid and the like.

The dissolution aids, for example ethers such as dimethyl (diethyl)glycol, dimethyl(diethyl)diglycol or tetrahydrofuran, ketones such as methyl ethyl ketone, acetone or cyclohexanone, esters such as butyl acetate, ethylglycol acetate or methylglycol acetate, methoxypropyl acetate, alcohols such as ethanol, propanol or butanol are used, if at all, only in very low amounts for reasons of environmental protection, usually not exceeding 10, preferably 1 to 5% by weight relative to water (as the main diluent). The amount of water in the aqueous coating composition is in most cases 15 to 80% by weight, preferably 30 to 60% by weight, relative to the entire coating composition.

The aqueous coating compositions are prepared using conventional methods of paint production as can be seen from the standard recipe given below.

The aqueous coating composition which is infinitely dilutable with water and whose overall solids content (125°C/2 hours) is generally 35 to 75, preferably 40 to 60% by weight, is applied in a known manner, for example by spraying using the compressed air process or by airless or electrostatic spraying processes. To cure the layers applied, temperatures of 120 to 200°C, preferably 150 to 170°C, are generally applied. The curing time is generally 15 to 30 minutes, preferably 18 to 20 minutes.

The crosslinked coatings thus obtained are distinguished in particular by improved stone chip resistance at low temperatures (0°C to -30°C) and by good interlayer adhesion. Moreover, they have good elongation at break and excellent impact resistance. The resistance to atmospheric humidity and solvents is also very good.

In the following examples, there are described several preferred embodiments to illustrate the invention. However, it should be understood that the invention is not intended to be limited to the specific embodiments.

EXAMPLE 1

A mixture was prepared from 235 g of a polyester of molecular weight 840 prepared from adipic acid, 1,6-hexanediol, neopentylglycol and 42.9 g of dimethylolpropionic acid and 75 g of N-methylpyrrolidone and the mixture was heated to 100°C. The clear solution was cooled to about 60°C, and then 121.8 g of a mixture of 2,4- and 2,6-toluylene diisocyanate were added dropwise at this

temperature at such a rate that the temperature did not exceed 65°C to 70°C. Stirring at this temperature was then continued until the isocyanate value had reached 1.6% (=2 isocyanato groups per molecule). 29.5 g of trimethylolpropane were than added, during which the system remained readily stirrable. After neutralization with 22.4 g of dimethylethanolamine, the finished polyurethane resin was dispersed by adding 590 g of deionized water to obtain a clear, approximately 40% strength dispersion having a viscosity of 1500 mPas.

EXAMPLE 2

235.6 g of a polyester with a molecular weight of 1020 prepared from adipic acid, 1,6-hexanediol and neopentyglycol were mixed with 56.0 g of polytetrahydrofuran (M = 1000), 42.9 g of dimethylolpropionic acid and 75 g of N-methylpyrrolidone and the mixture was reacted as described in Example 1 with toluylene diisocyanate (mixture of isomers). After reaction of the prepolymer with glycerol, the mixture was neutralized with 22.8 g of dimethylethanolamine, and the resin was dispersed in 620 g of deionized water.

EXAMPLE 3

317.1 g of a polyester with a molecular weight of 1130 prepared from adipic acid, hexanediol, neopentyglycol and terephthalic acid were mixed with 42.9 g of dimethylolpropionic acid and 90 g of N-methylpyrrolidone and the mixture was heated to 100°C. After cooling to 65°C, 183.7 g of 4,4'-diisocyanatodicylcohexylmethane (Desmodur W) were added dropwise and the reaction batch was then maintained at 80°C until the calculated isocyanate value of 1.33 % (=2 isocyanato groups per molecule) had been reached. 80.4 g of

tr_ethylolpropane and then 22.8 g of dimethylethanolamine were added and stirring of the mixture was continued for 20 minutes. The polyurethane resin was then dispersed by adding 700 g of deionized water.

STANDARD RECIPE FOR SURFACER FORMULATION

58.0 parts of the binder from Example 1 to 3 were dispersed with 4.0 parts of a commercially available melamine/formaldehyde condensation product, 13.3 parts of titanium dioxide, 13.2 parts of barium sulfate (Blanc fix micro), 0.1 part of carbon black, 11.1 parts of deionized water and 0.3 parts of conventional paint additives in a pearl mill for 20 minutes at 6000 rpm to form the surfacer composition which was applied to a zinc-phosphated steel sheet coated to about 30 µm with a cathodically deposited electroprimer with a compressed air gun. The curing of the surfacer was carried out in a through-circulation oven at 80°C for 10 minutes and then at 160°C for 20 minutes to obtain a dry film thickness of 35 ± 2 µm. A commercially available alkyd/melamine automotive paint was applied on top of the surfacer coat and baked at 130°C for 30 minutes for dry film thickness of about 30± 5 µm. The test results are summarized in Table I below and the stabilities of the films (resistance to solvents and water) are those required in commercial practice.

APPEARANCE OF THE TOPCOAT

Gloss and surface of the topcoat on various surfacer materials were rated subjectively by a scale from 1 = very good to 5 = very poor.

STONE CHIP RESISTANCE

Tested by the stone chip testing apparatus of VDA (from Erichsen, type 508). For this test, the test specimens were

bombarded in each case with 1 kg of steel shot (angular, 4-5 mm) accelerated by compressed air (2 bar). By comparison with control specimens, topcoat adhesion (0 = no chipping off from surfacer, 10 = complete delamination) and penetrations down to the metal (0 = no penetration, 10 = a large number of penetrations) were rated.

TABLE 1

Example	1	2	3
Appearance of the topcoat	2 - 3	2	2
Topcoat adhesion			
+ 20°C	1 - 2	1	2 - 3
- 20°C	1 - 2	1 - 2	2 - 3
Penetrations			
+ 20°C	1	1	2
- 20°C	1	2	3
Crosshatch (according to DIN 53151)	ch 0	ch 0	ch 0

Various modifications of the compositions and process of the invention may be made without departing from the spirit or scope thereof and it is to be understood that the invention is intended to be limited only as defined in the appended claims.

1. An aqueous coating composition for preparing primers or primer surfacers containing at least one water-dispersible binder resin, and crosslinking agents and optionally conventional additives, wherein at least some of the water-dispersible binder resin is a polyurethane resin containing structural units derived from

(A) polyisocyanates,

(B) polyols having an average molecular weight $\bar{M}_n$ of at least 400,

(C) optionally low-molecular-weight polyols,

(D) compounds having at least two groups which are reactive toward isocyanato groups and at least one group which is capable of anion formation,

(E) polyols carrying no other groups which are reactive with isocyanato groups, these structural units (E) being in each case at the chain end of the polyurethane resin,

(F) optionally compounds which are monofunctional or contain active hydrogen of varying reactivity and are different from (E), these structural units (F) likewise being at the chain end of the polyurethane resin and

(G) optionally compounds which are different from (B), (C), (D), (E) and (F) and contain at least two groups which are reactive with NCO groups.

2. A coating composition of claim 1 wherein the amount of polyurethane resin in the aqueous surfacer composition is 5 to 40% by weight, relative to the entire surfacer composition.

3. A coating composition of claim 1 wherein the aqueous surfacer composition additionally contains at least one further binder in an amount of up to 60% by weight, relative to the polyurethane resin.

4. A coating composition of claim 2 wherein the aqueous surfacer composition additionally contains at least one further binder in an amount of up to 60% by weight, relative to the polyurethane resin.

5. A coating composition of claim 1 which contains 10 to 35% by weight, relative to the sum of the binder to be crosslinked and a crosslinking agent, of water-compatible amino resins as crosslinking agent.

6. A coating composition of claim 1 wherein the polyurethane resin has an average molecular weight $\overline{M}_n$ of 2,000 to 6,000.

7. A coating composition of claim 1 wherein the hydroxyl number of the polyurethane resin is 30 to 80.

8. A coating composition of claim 1 wherein the amount of structural unit(A) is 10 to 50% by weight, structural unit (B) is 15 to 80% by weight, structural unit (C) is 0 to 20% by weight, structural unit(D) is 2 to 20% by weight and structural unit(E) is 2 to 25% by weight , each relative to the polyurethane resin.

9. A coating composition of claim 1 wherein structural unit (B) is derived from polyether or polyester polyols having an average molecular weight $\overline{M}_n$ of 400 to 5,000.

10. A coating composition of claim 1 wherein the compounds of (D) are polyols containing at least one carboxyl group.

11. A coating composition of claim 10 wherein (D) is an α,α-dimethylolalkanoic acid.

12. A coating composition of claim 1 wherein the compounds of (E) are glycerol or trimethylolpropane.

13. A coating composition of claim 1 wherein the compounds of (F) are monoamines additionally containing at least one OH group.

14. A coating composition of claim 1 wherein the compounds of (G) are water, hydrazine or diamines which optionally contain OH groups.

15. A process for the preparation of a coating composition of claim 1 comprising preparing a polyurethane prepolymer from the polyisocyanates of (A), the polyols of (B) and optionally the low-molecular-weight polyols of (C) and the compounds of (D) which prepolymer contains on average at least 1.7, free isocyanato groups per molecule, reacting the prepolymer with an excess of the compounds of (E) optionally in a mixture with (F) and/or (G) in a non-aqueous system, and then optionally neutralizing the completely reacted polyurethane resin and then transferring it into an aqueous system, the further optionally binder resins, the crosslinking agent and the conventional additives added before, during, or after the preparation of the polyurethane resin.

16. The process of claim 15 wherein the prepolymer contains 2 to 2.5 free isocyanato groups per molecule.

17. The process of claim 15 wherein the compounds of (E) are used in such an amount that the equivalent ratio of NCO groups of the prepolymer which previously may already have been reacted with the compounds of (F) and/or (G), to reactive groups of (E) is 1:1.1 to 1:5.

18. The process of claim 15 wherein the amount of (F) and/or (G) is 0 to 90 %, relative to (E).

19. A primer or primer surfacer containing an effective amount of an aqueous coating composition of claim 1.

20. A substrate coated with a primer or primer surfacer of claim 19.

21. A coated substrate of claim 20 which substrate is an automotive body.

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AQUEOUS COATING COMPOSITION, ITS PREPARATION AND USE

ABSTRACT OF THE DISCLOSURE

Aqueous coating compositions for preparing primers or primer surfacers containing at least one water-dispersible binder resin and crosslinking agents and optionally conventional additives, wherein at least some of the water-dispersible binder resin is a polyurethane resin containing structural units derived from

(A) polyisocyanates,

(B) polyols having an average molecular weight $\overline{M}_n$ of at least 400,

(C) optionally low-molecular weight polyols,

(D) compounds having at least two groups which are reactive toward isocyanato groups and at least one group which is capable of anion formation,

(E) polyols carrying no other groups which are reactive with isocyanato groups, these structural units (E) being in each case at the chain end of the polyurethane resin,

(F) optionally compounds which are monofunctional or contain active hydrogen of varying reactivity and are different from (E), these structural units (F) likewise being at the chain end of the polyurethane resin and,

(G) optionally compounds which are different from (B), (C), (D), (E) and (F) and contain at least two groups which are reactive with NCO groups.

The primer surfacers obtainable therefrom are distinguished, inter alia, by improved stone chip resistance at low temperatures and by good interlayer adhesion, while the corresponding primers show improved corrosion protection.

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